Silver-promoted site-selective intramolecular cyclization of 2-methylthiobenzamide through α-C(sp^3)–H functionalization

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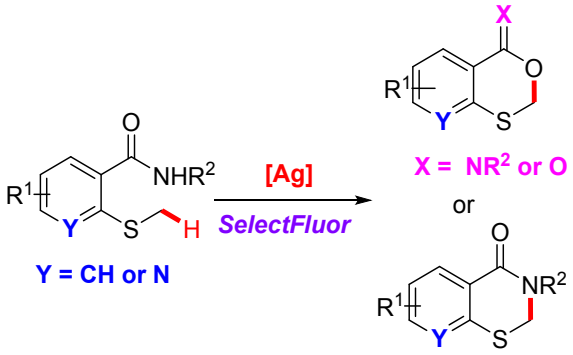
Graphical Abstract



Abstract Silver-mediated intramolecular α-C(sp^3)–H bond functionalization of the methylthio group has been established in the presence of Selectfluor as an additive. This novel strategy

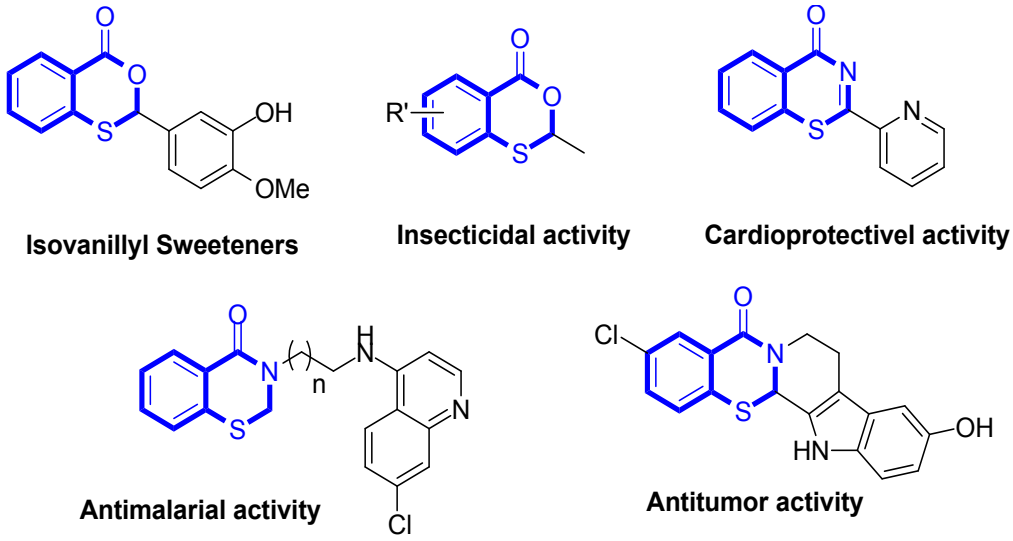
This is the author's manuscript of the article published in final edited form as:
Yang, K., Niu, B., Ma, Z., Wang, H., Lawrence, B., & Ge, H. (2019). Silver-promoted site-selective intramolecular cyclization of 2-methylthiobenzamide through α-C(sp3)–H functionalization. The Journal of Organic Chemistry. https://doi.org/10.1021/acs.joc.9b02202

provides an efficient access to various diverse sulfur-based heterocycles with good yields and functional group compatibility. It is noteworthy that the completely novel benzooxathiin-4-imine skeletons were reported for the first time in this study.

INTRODUCTION

Transition metal-promoted direct C–H bond functionalization has been regarded as one of the most efficient and straightforward approaches for selective carbon-carbon and carbon-heteroatom bond construction.[1] Within this reaction category, the α-C–H bond functionalization of a sulfide group is highly challenging and has met with only limited success to date,[2] probably due to their facile oxidation to sulfoxides or sulphones[3] and their strong coordination ability to transition metals.[4] Therefore, development of a novel and highly efficient method for the transition metal-promoted α-C–H bond functionalization of a sulfide group would be of great significance.

Figure 1. The selected biologically active compounds containing sulfide heterocyclic skeletons



Sulfur-containing heterocyclic skeletons, including benzooxathiin-4-ones and benzothiazin-4-ones, have received tremendous attention because of their vital use in a large number of bioactive natural products, pharmaceuticals, and food additives (Figure 1).[5] Extensive efforts have been attempted to develop novel methods for the construction of these compounds.[6-9] However, these methods often provided only one type of sulfur-based heterocycle[6b, 7b, 8, 9] or suffered from the use of odour smelling thiophenol derivatives,[7] sensitive acyl chlorides,[8] or multi-step preparation of starting materials,[9] which limited the general applicability. Herein, we demonstrated silver and selectfluor promoted site-selective intramolecular α-C(sp^3)–H bond functionalization of the unactivated methylthio group to access diverse sulfur-based heterocycles. To the best of our knowledge, this process provides the first example of site-selective intramolecular cyclization of 2-methylthiobenzamides to construct structurally novel benzooxathiin-4-imine skeletons which could have potential biological activities.

RESULTS AND DISCUSSION

Table 1. Optimization of reaction conditions for benzooxathiin-4-imine **2a** [a]

1a **2a**

Entry	[Ag] (eq.)	Additives (eq.)	Base (eq.)	Yield (%)[b]
1	$AgNO_3$(20)	Selectfluor (1.0)	NaOAc (1.5)	26
2	AgTFA (20)	Selectfluor (1.0)	NaOAc (1.5)	15
3	AgF (20)	Selectfluor (1.0)	NaOAc (1.5)	25
4	AgOTf (20)	Selectfluor (1.0)	NaOAc (1.5)	20
5	AgOAc (20)	Selectfluor (1.0)	NaOAc (1.5)	35
6	Ag_2CO_3 (20)	Selectfluor (1.0)	NaOAc (1.5)	24
7	Ag_2O (20)	Selectfluor (1.0)	NaOAc (1.5)	41
8	AgO (20)	Selectfluor (1.0)	NaOAc (1.5)	33
9	Ag_2O (20)	Selectfluor (1.0)	KOAc (1.5)	15
10	Ag_2O (20)	Selectfluor (1.0)	Na_2CO_3 (1.5)	20
11	Ag_2O (20)	Selectfluor (1.0)	K_2CO_3 (1.5)	26
12	Ag_2O (20)	Selectfluor (1.0)	Cs_2CO_3 (1.5)	30
13	Ag_2O (20)	NFSI (1.0)	NaOAc (1.5)	28
14	Ag_2O (20)	NFPT (1.0)	NaOAc (1.5)	23
15	Ag_2O (50)	Selectfluor (1.0)	NaOAc (1.5)	73 (71)[c]
16	-	Selectfluor (1.0)	NaOAc (1.5)	0
17	Ag_2O (50)	-	NaOAc (1.5)	0
18	Ag_2O (50)	Selectfluor (1.0)	-	10

[a]Reaction conditions: **1a** (54.28 mg, 0.2 mmol), Ag source, additive, base, DCE (3.0 mL), 140 °C, 4 h. [b]Yields are based on **1a**, determined by ^{1}H-NMR using dibromomethane as the internal standard. [c]Isolated yields. NFSI = *N*-Fluorobenzenesulfonimide. NFPT = 1-Fluoro-2,4,6-trimethylpyridinium triflate.

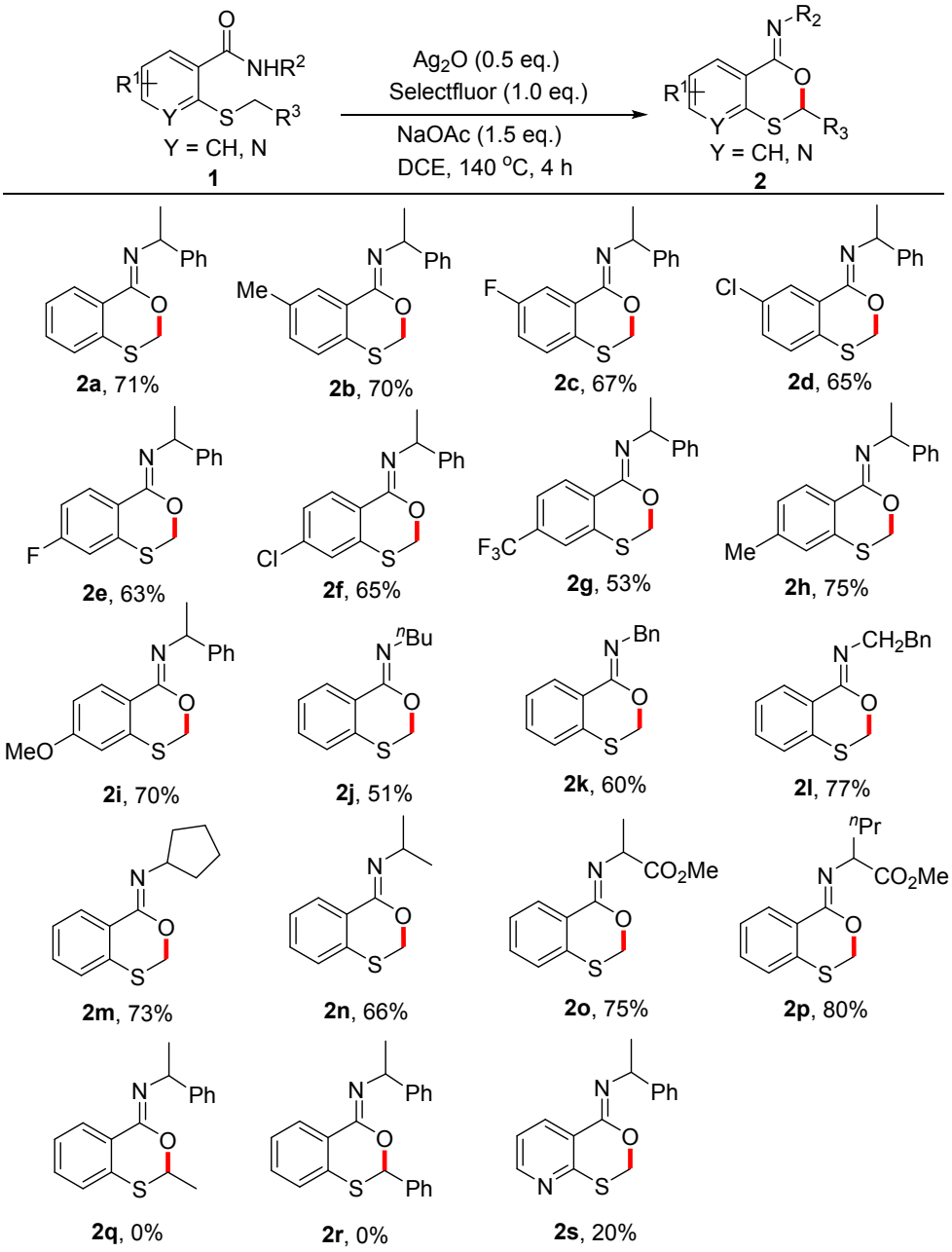
Our investigation began with the intramolecular C–H bond functionalization of 2-(methylthio)-*N*-(1-phenylethyl)benzamide (**1a**) in the presence of catalytic $AgNO_3$ and stoichiometric amounts of Selectfluor with NaOAc in DCE at 140 °C. The desired product **2a** was detected in

26% yield (Table 1, entry 1). The subsequent examination of different silver catalysts revealed that this process could be promoted by Ag_2O with an improved yield (entries 1-8). Next, various kinds of bases were examined in this process, and it turned out that NaOAc was the optimal base (entries 9-12). Additionally, the screening of other additives revealed that a low yield was observed with *N*-fluorobenzenesulfonimide (NFSI) or 1-fluoro-2,4,6-trimethylpyridinium triflate (NFPT) (entries 13-14). To our delight, it was found that the yield of desired product **2a** was improved to 73% by increasing the amounts of Ag_2O from 20 to 50 mol% (entry 15). The control experiments demonstrated that no desired product **2a** was observed in the absence of a silver catalyst or additive (entries 16-17). Finally, in the absence of any base additives, only a low yield of product **2a** was obtained (entry 18).

With the optimized reaction conditions in hand, we carried out the intramolecular cyclization reaction of 2-methylthiobenzamides to synthesize benzooxathiin-4-imine derivatives. As shown in Table 2, both electron-donating (Me and MeO) and electron-withdrawing groups (F, Cl, Br and CF_3) on the phenyl ring of 2-methylthiobenzamides were all compatible with the current reaction system, and the desired products (**2a**-**i**) were isolated in good yields. Then, the substrate scope study of *N*-substituted 2-methylthiobenzamides was examined. The linear *N*-substituted substrates **1j**-**l** provided the corresponding products **2j**-**l** in good yields. As

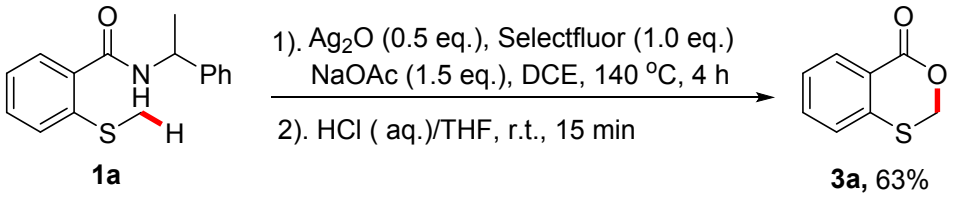
expected, cyclopentyl substituted substrate **1m** generated the corresponding product **2m** in 63% yield. Furthermore, isopropyl substituted substrate **1n** could also be transformed to the product **2n** in 66% yield. It was noteworthy that an ester group was well tolerated, and products **2o** and **2p** were obtained in good yields. Unfortunately, substrates bearing an ethyl or benzyl group on the sulfur atom failed to provide desired products (**2q-r**). The pyridine-containing substrate **1s** also provided the desired product **2s** in 20% isolated yield. Besides, we found that the imine group on the product of **2a** can be easily removed to yield 4*H*-benzo[*d*][1,3]oxathiin-4-one **3a** under the acidic conditions (Scheme 1).

Table 2. The reaction of 2-methylthiobenzamide for the synthesis of benzooxathiin-4-imine [a,b]



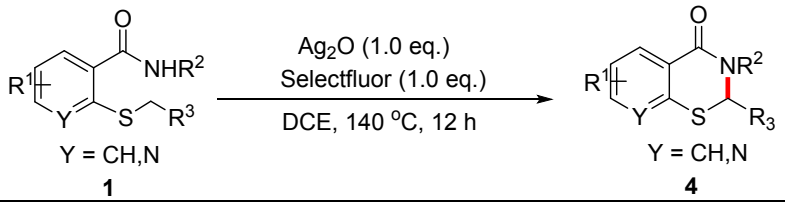
Reaction conditions: **1** (0.2 mmol), Selectfluor (70.85 mg, 0.2 mmol), Ag_2O (23.17 mg, 0.1 mmol), NaOAc (24.61 mg, 0.3 mmol), DCE (3.0 mL), 140 °C, 4 h, isolated yields.

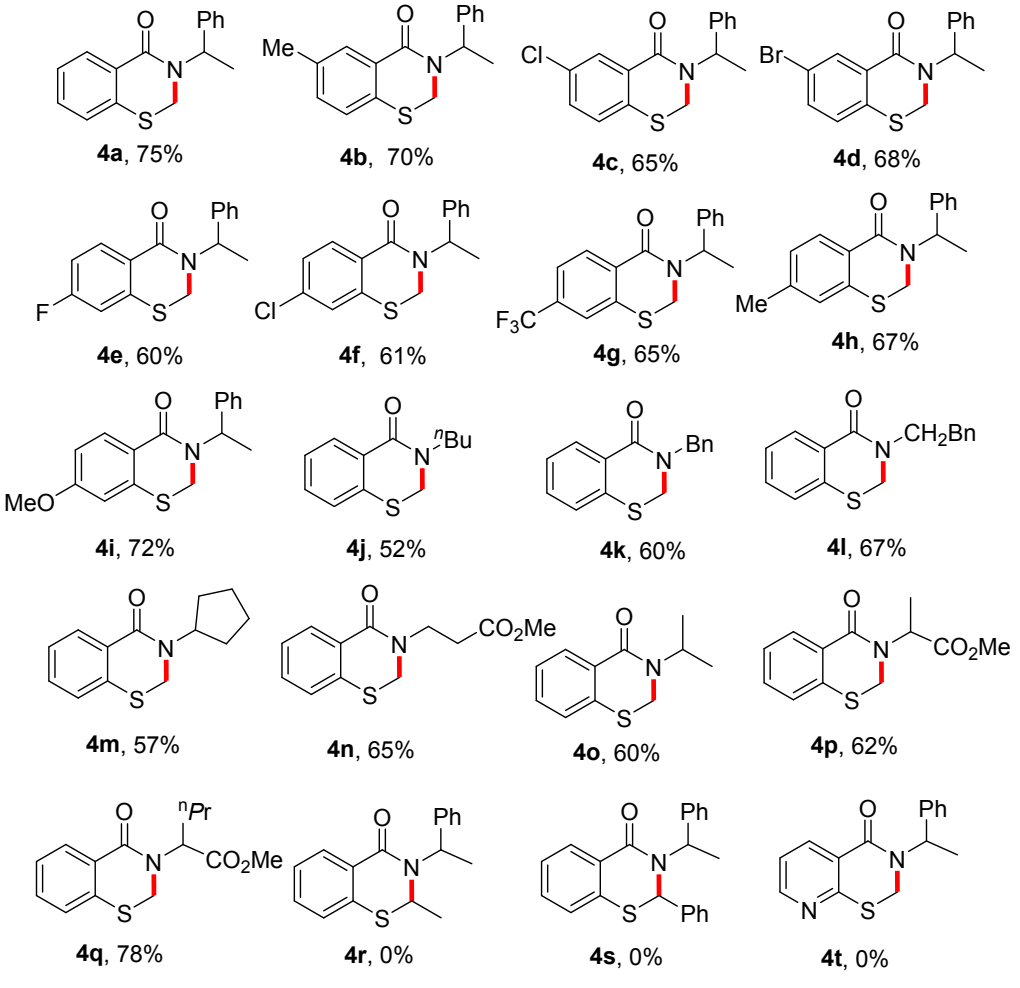
Scheme 1. The reaction of 2-methylthiobenzamide for the synthesis of benzooxathiin-4-one **3a**



1a **3a,** 63%

Table 3. The reaction of 2-methylthiobenzamide for the synthesis of benzothiazin-4-one [a,b]





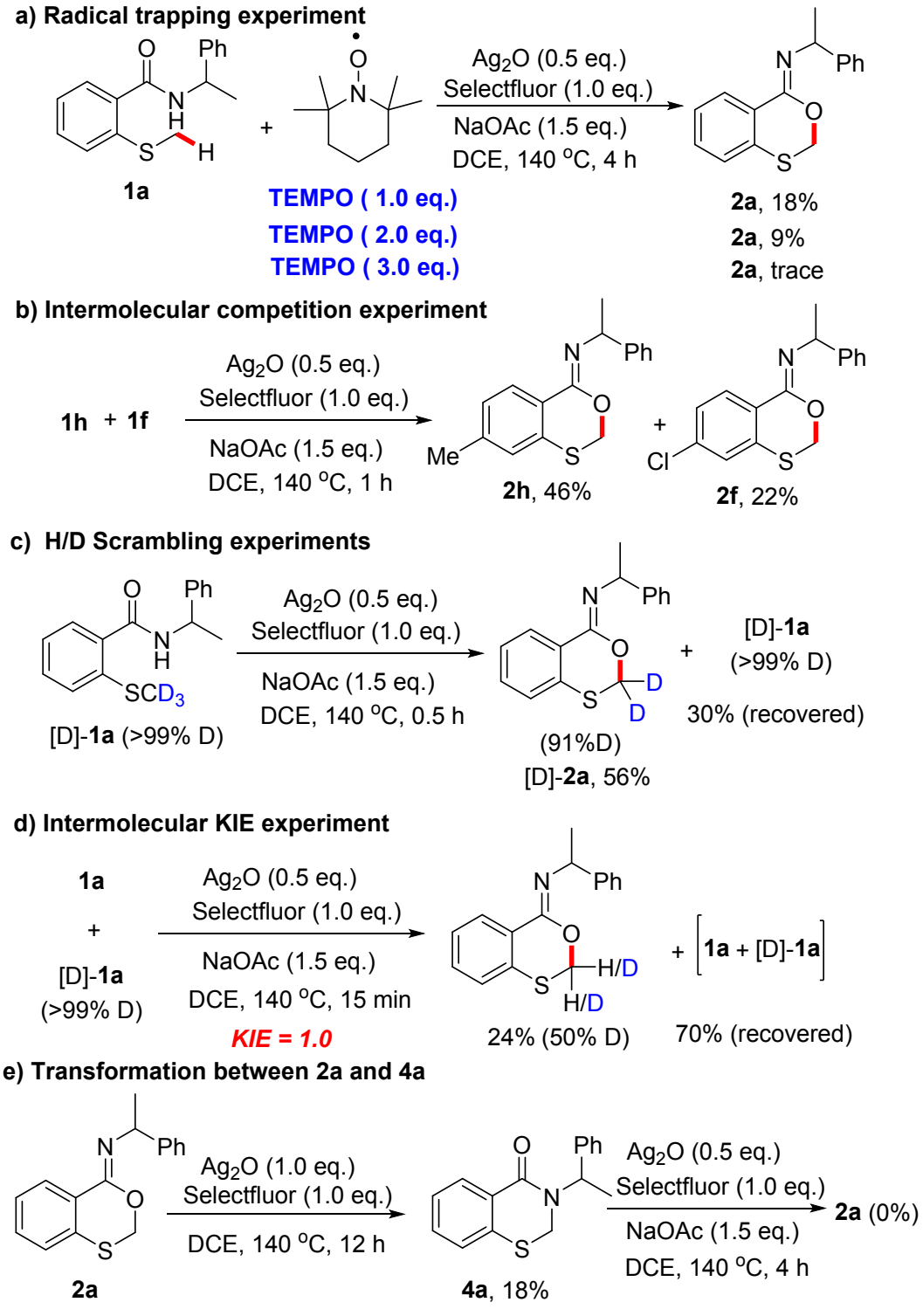
[a] Reaction conditions: **1** (0.2 mmol), Selectfluor (70.85 mg, 0.2 mmol), Ag_2O (46.34 mg, 0.2 mmol), DCE (3.0 mL), 140 °C, 12 h. [b]Isolated yields.

Next, we explored the intramolecular cyclization reaction of 2-methylthiobenzamides for the synthesis of benzothiazin-4-ones, and only 20% yield of the desired product **4a** was isolated under the standard conditions by extending reaction time to 12 hours. Further screening of reaction conditions indicated that the reaction of **1a** could produce the desired product **4a** with 75% isolated yield in the presence of stoichiometric amounts of Ag_2O without NaOAc (see Table S1 in Supporting Information). As expected, various kinds of substituted 2-methylthiobenzamides were well tolerated under the modified conditions, providing the desired products (**4b-q**) in moderate to good yields. However, no desired products (**4r-s**) could be obtained when the methyl group on the sulfur atom was replaced with another alkyl group. Furthermore, the pyridine-containing substrate **1s** could not afford the corresponding product **4t** under the current conditions (Table 3).

To provide some insights into the reaction mechanism, a series of control experiments were carried out (Scheme 2). First, several radical trapping experiments were performed, and the results showed that the addition of TEMPO resulted in the decreased yield of **2a**, suggesting that a single electron transfer (SET) may be involved in this process (Scheme 2a). Next, a competition experiment was carried out between **1h** and **1f**, and it turned out that the reaction is favored with an electron-donating group on the aromatic ring of 2-methylthiobenzamide (Scheme 2b). Furthermore, no obvious H/D exchange was observed when this reaction was performed with an isotopically labeled substrate (Scheme 2c). The KIE experiment of **1a** showed that a 2nd order of kinetic isotope effect was observed, suggesting that the cleavage of the C(sp^3)–H bond of the methyl sulfide group might not be involved in the rate-

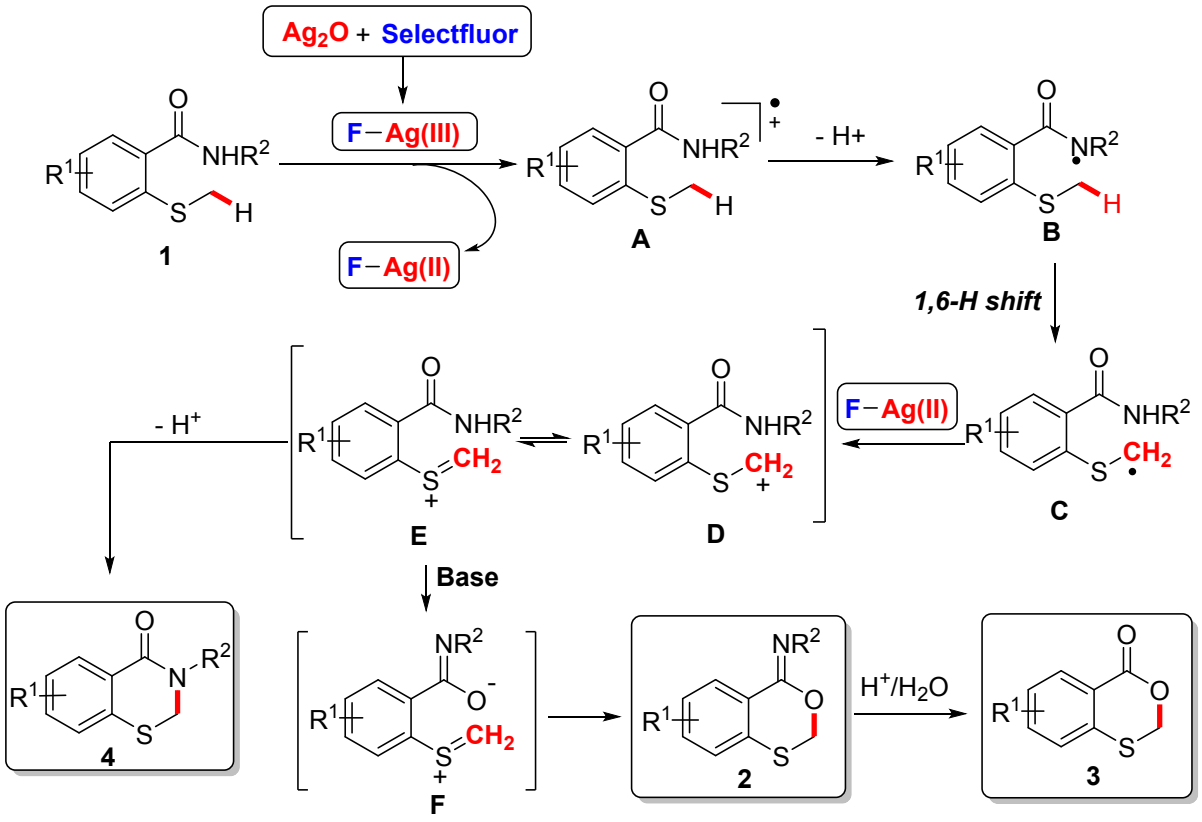
determining step (Scheme 2d). Finally, the transformation experiments between **2a** and **4a** indicated that benzooxathiin-4-imine **2a** can be converted to benzothiazin-4-one **4a** in 18% yield under the reaction conditions for preparing **4a** (Scheme 2e).

Scheme 2. Mechanistic Studies



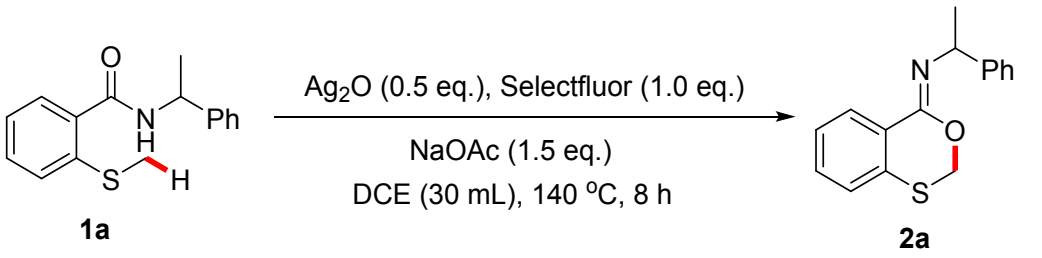
Based on the above results and previous literatures,[10-13] a plausible reaction pathway to construct product **2** is proposed in Scheme 3. First, oxidation of Ag(I) by Selectfluor generates the F−Ag(III) intermediate through oxidative insertion.[10a] Then, the F−Ag(III) species undergoes a single electron oxidation to 2-methylthiobenzamide **1** to give the Ag(II)−F intermediate and radical cations **A**.[10b] Deprotonation of **A** gives the amidyl radical **B**, which immediately induces a 1,6-H radical shift to afford the carbon-centered radical **C**.[11] Subsequently, radical **C** can be oxidized to the corresponding carbocation **D** and its isomer **E**.[12] Then, intermediate **E** affords the desired product **4** through a sequential intramolecular cyclization and deprotonation process. Furthermore, in the presence of base, intermediate **E** can be easily transformed to intermediate **F** and produce the product **2**, which can be further converted to the product **3** via a hydrolytic process.[13]

Scheme 3. A possible catalytic cycle



In order to illustrate the synthetic utility of this novel method, a larger scale reaction for the synthesis of benzooxathiin-4-imine **2a** was carried out (Scheme 4). When 2-(methylthio)-*N*-(1-phenylethyl)benzamide **1a** (0.54 g, 2 mmol) was treated with 0.5 equivalent of Ag_2O, 1.0 equivalent of Selectfluor and 1.5 equivalents of NaOAc in DCE (30 mL) at 140 °C, the desired product **2a** was obtained in 62% isolated yield.

Scheme 4. The larger scale reaction for the synthesis of benzooxathiin-4-imine **2a**



1a

2 mmol, 0.54 g

2a

62% isolated yield

In summary, an efficient site-selective intramolecular cyclization of 2-methylthiobenzamides has been developed through a silver and Selectfluor-promoted C−H bond functionalization process. This method affords various important sulfur-containing heterocyclic derivatives, including benzooxathiin-4-imines, benzooxathiin-4-ones, and benzothiazin-4-ones. Further study on the detailed reaction mechanism and application is ongoing in our laboratories.

EXPERIMENTAL SECTION

General. All the solvents and commercially available reagents were purchased from commercial sources and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE Ⅲ–300, 400 or 500 spectrometers. ^{1}H NMR data were reported as chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI).

Materials. 2-Methylthiobenzamides **1** were prepared from corresponding 2-thiobenzoic acid (2.0 mmol) and amines (3.0 mmol) in DCM at room temperature according to the reported procedure.[14,15]

General procedures for the synthesis of product 2. A 50 mL Schlenk tube was charged with 2-methylthiobenzamide **1** (0.2 mmol), Ag_2O (23.17 mg, 0.1 mmol), Selectfluor (70.85 mg, 0.2 mmol), NaOAc (24.61 mg, 0.3 mmol), and DCE (3.0 mL). The tube was then sealed in the heating mantle and stirred vigorously at 140 ˚C for 4 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL) and filtered through a pad of Celite. The filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2** by using mixed petroleum ether and ethyl acetate (v / v = 50:1).

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine (**2a**)* : Colourless oil, 38.2 mg, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.30 – 7.23 (m, 3H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.15 (q, *J* = 6.6 Hz, 1H), 1.50 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.2, 146.4, 135.1, 130.4, 130.3, 128.3, 127.9, 127.8, 126.6, 126.5, 126.4, 68.4, 54.7, 24.7. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947, found: 270.0950.

*(6-Methyl-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine (**2b**)*: Colourless oil, 39.6 mg, yield: 70%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.22 – 7.17 (m, 2H), 5.27 – 5.15 (m, 3H), 2.41 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.9, 146.5, 136.5, 131.7, 131.4, 130.6, 128.3, 127.8, 127.5, 126.6, 126.4, 68.5, 54.6, 24.6, 21.2. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104, found: 284.1106.

*(6-Fluoro-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine (**2c**)* :. Colourless oil, 38.5 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 9.7, 2.8 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.11 (td, *J* = 8.3, 2.8 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.22 (d,

J = 10.4 Hz, 1H), 5.15 (q, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 245.5 Hz), 149.2, 146.2, 130.3 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 7.7 Hz), 129.4 (d, *J* = 7.6 Hz), 128.4, 126.67, 118.1 (d, *J* = 22.9 Hz), 117.0 (d, *J* = 24.4 Hz), 68.6, 54.9, 24.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.5 (s). HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}FNOS$ $[M+H]^+$: 288.0853, found: 288.0852.

N-(6-Chloro-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine ***(2d)*** : Colourless oil, 39.4 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.3 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.30 – 7.23 (m, 2H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.14 (q, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.0, 146.2, 133.5, 132.3, 130.4, 130.0, 129.1, 129.0, 128.4, 126.6, 68.4, 54.9, 24.6. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}ClNOS$ $[M+H]^+$: 304.0557, found: 304.0558.

N-(7-Fluoro-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine ***(2e)*** : Colourless oil, 36.2 mg, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.06 – 6.95 (m, 2H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.14 (q, *J* = 6.6 Hz, 1H), 1.50 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 253.9 Hz), 149.4, 146.4, 137.4 (d, *J* = 9.5 Hz), 132.8 (d, *J* = 9.1 Hz), 128.3, 126.6, 126.5, 123.9 (d, *J* = 3.2 Hz), 114.4 (d, *J* = 23.9 Hz), 114.2 (d, *J* = 21.9 Hz), 68.3, 54.79, 24.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.2 (s). HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}FNOS$ $[M+H]^+$: 288.0853, found: 288.0855.

N-(7-Chloro-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine ***(2f)*** : Colourless oil, 39.4 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.24 (m, 3H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 5.14 (q, *J* = 6.6 Hz, 1H), 1.50 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.4, 146.3, 136.7, 136.5, 131.7, 128.3, 127.4, 126.9, 126.55, 126.53, 126.05, 68.29, 54.79, 24.64. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}ClNOS$ $[M+H]^+$: 304.0557, found: 304.0557.

*1-Phenyl-N-(7-(trifluoromethyl)-4H-benzo[d][1,3]oxathiin-4-ylidene)ethanamine (**2g**)* : Colourless oil, 35.7 mg, yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.16 (q, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.0, 146.1, 136.2, 132.1 (q, *J* = 32.9 Hz), 131.0, 130.7, 128.4, 126.6, 126.5, 124.9 (q, *J* = 3.9 Hz), 123.4 (q, *J* = 272.7 Hz), 122.9 (q, *J* = 3.6 Hz), 68.3, 55.0, 24.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.2 (s). HRMS (ESI, *m/z*): calcd. for $C_{17}H_{15}F_3NOS$ $[M+H]^+$: 338.0821, found: 338.0818.

*N-(7-Methyl-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine (**2h**)* : Colourless oil, 42.5 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.15 – 7.06 (m, 2H), 5.26 (d, *J* = 10.4 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.15 (q, *J* = 6.6 Hz, 1H), 2.39 (s, 3H), 1.51 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 146.7, 140.8, 134.9, 130.3, 128.25, 128.1, 127.6, 126.6, 126.4, 125.0, 68.4, 54.6, 24.7, 21.3. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104, found: 284.1106.

*N-(7-methoxy-4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylethanamine (**2i**)* : Colourless oil, 41.9 mg, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 1H), 6.85 – 6.78 (m, 2H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 5.13 (q, *J* = 6.6 Hz, 1H), 3.86 (s, 3H), 1.50 (d, *J* = 6.6 Hz, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 150.1, 146.8, 136.6, 132.1, 128.2, 126.6, 126.3, 120.3, 113.6, 111.7, 68.3, 55.5, 54.5, 24.7. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1053, found: 300.1056.

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)butan-1-amine (**2j**)* : Colourless oil, 22.5 mg, yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.36 – 7.24 (m, 3H), 5.25 (s, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.49 – 1.43 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 135.0, 130.1, 130.0, 127.9, 127.8, 126.5, 68.4, 46.4, 33.0, 20.8, 14.0. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{16}NOS$ $[M+H]^+$: 222.0947, found: 222.0951.

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)-1-phenylmethanamine (**2k**)* : Colourless oil, 30.6 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.25 (m, 6H), 5.30 (s, 2H), 4.69 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.8, 140.8, 135.0, 130.4, 130.3, 128.3, 127.9, 127.7, 127.6, 126.5, 126.5, 68.5, 50.4. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791, found: 256.0792.

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)-2-phenylethanamine (**2l**)* : Colourless oil, 41.4 mg, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.18 (m, 1H), 7.36 – 7.21 (m, 8H), 5.14 (s, 2H), 3.73 – 3.70 (m, 2H), 3.00 – 2.96 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.6, 140.9, 135.1, 130.3, 130.0, 129.0, 128.2, 127.9, 127.5, 126.5, 125.9, 68.3, 48.5, 37.3. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947, found: 270.0948.

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)cyclopentanamine (**2m**)* : Colourless oil, 34.0 mg, yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.36 – 7.24 (m, 3H), 5.25 (s, 2H), 4.27 – 4.22 (m, 1H), 2.00 – 1.91 (m, 2H), 1.86 – 1.77 (m, 2H), 1.68 – 1.53 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3, 135.0, 130.2, 130.0, 127.9, 126.5, 68.4, 56.8, 34.3, 24.5. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{16}NOS$ $[M+H]^+$: 234.0947, found: 234.0950.

*N-(4H-benzo[d][1,3]oxathiin-4-ylidene)propan-2-amine (**2n**)* : Colourless oil, 27.3 mg, yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.36 – 7.24 (m, 3H), 5.24 (s, 2H), 4.16 – 4.07 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.8, 135.1, 130.2, 130.1, 127.9, 126.5, 68.4, 46.4, 23.8. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}NOS$ $[M+H]^+$: 208.0791, found: 208.0792.

*Methyl 2-((4H-benzo[d][1,3]oxathiin-4-ylidene)amino)propanoate (**2o**)* : Colourless oil, 37.6 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38 – 7.25 (m, 3H), 5.24 (s, 2H), 4.63 (q, *J* = 6.9 Hz, 1H), 3.75 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 152.7, 135.2, 130.7, 130.6, 127.8, 127.0, 126.6, 68.5, 54.3, 52.1, 19.1. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{13}NNaO_3S$ $[M+Na]^+$: 274.0508, found: 274.0507.

*Methyl 2-((4H-benzo[d][1,3]oxathiin-4-ylidene)amino)pentanoate (**2p**)* : Colourless oil, 44.6 mg, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.25 (m, 3H), 5.26 – 5.20 (m, 2H), 4.54 (dd, *J* = 7.9, 5.6 Hz, 1H), 3.74 (s, 3H), 1.90 – 1.80 (m, 2H), 1.43 – 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.7, 152.9, 135.2, 130.7, 130.7, 127.9, 127.1, 126.6, 68.5, 58.8, 51.9, 36.0, 19.4, 13.9. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{17}NNaO_3S$ $[M+Na]^+$: 302.0821, found: 302.0823.

*N-(1-phenylethyl)-4H-[1,3]oxathiino[4,5-b]pyridin-4-imine (**2s**)* : Colourless oil, 10.8 mg, yield: 20%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.41 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.28 – 7.24 (m, 2H), 7.18 – 7.09 (m, 2H), 5.23 (q, *J* = 10.7 Hz, 2H), 5.04 (q, *J* = 6.6 Hz, 1H), 1.38 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ. 157.10, 151.00, 149.44, 146.19, 137.92, 128.50, 126.78, 126.68, 124.59, 121.48, 68.18, 55.31, 24.72. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{15}N_2OS$ $[M+H]^+$: 271.0900, found: 271.0905.

General procedures for the synthesis of product 3a. A 50 mL Schlenk tube was charged with 2-methylthiobenzamide **1a** (54.28 mg, 0.2 mmol), Ag_2O (23.17 mg, 0.1 mmol), Selectfluor (70.85 mg, 0.2 mmol), NaOAc (24.61 mg, 0.3 mmol) and DCE (3.0 mL). The tube was then sealed in the heating mantle and stirred vigorously at 140 ˚C for 4 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. After that, the residue was dissolved in 50 mL Schlenk tube with THF (4.0 mL). Next, aqueous HCl (5.0 wt%, 0.5 mL) were added into the tube slowly. The reaction was stirred vigorously at room temperature for 15 min. Then the reaction mixture was diluted with DCM (15 mL) and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **3a** by using mixed petroleum ether and ethyl acetate (v / v = 10:1).

*4H-benzo[d][1,3]oxathiin-4-one (**3a**)* [16] : Colourless oil, 20.9 mg, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.36 (m, 2H), 5.46 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.3, 138.8, 133.5, 132.8, 127.7, 126.9, 124.5, 68.8.

General procedures for the synthesis of product 4. A 50 mL Schlenk tube was charged with 2-methylthiobenzamide **1** (0.2 mmol), Ag_2O (46.34 mg, 0.2 mmol), Selectfluor (70.85 mg, 0.2 mmol) and DCE (3.0 mL). The tube was then sealed in the heating mantle and stirred vigorously at 140 ˚C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **4** by using mixed petroleum ether and ethyl acetate (v / v = 10:1).

*3-(1-Phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one (**4a**)* : Colourless oil, 40.3 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.25 (m, 8H), 6.21 (q, *J* = 7.0 Hz, 1H), 4.45 (d, *J* = 12.9 Hz, 1H), 4.19 (d, *J* = 12.9 Hz, 1H), 1.66 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.7, 139.7, 137.2, 131.7, 131.0, 129.6, 128.7, 127.8, 127.5, 127.1, 126.1, 51.9, 43.7, 16.4. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947, found: 270.0945.

*6-Methyl-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one (**4b**)* : Colourless oil, 39.6 mg, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.21 (q, *J* = 7.0 Hz, 1H), 4.42 (d, *J* = 12.9 Hz, 1H), 4.17 (d, *J* = 12.9 Hz, 1H), 2.39 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.0, 139.8, 136.0, 133.7, 132.6, 131.4, 129.3, 128.7, 127.8, 127.4, 127.0, 51.8, 43.8, 21.0, 16.4. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104, found: 284.1106.

*6-Chloro-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one (**4c**)* : Colourless oil, 39.4 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.8 Hz, 1H), 7.45 – 7.33 (m, 6H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.18 (q, *J* = 7.0 Hz, 1H), 4.44 (d, *J* = 13.0 Hz, 1H), 4.18 (d, *J* = 13.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz,

3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.7, 139.4, 135.6, 132.2, 131.7, 130.9, 128.8, 128.4, 127.9, 127.4, 52.1, 43.7, 16.3. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}ClNOS$ $[M+H]^+$: 304.0557, found: 304.0559.

6-Bromo-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one ***(4d)*** : Colourless oil, 47.2 mg, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.2 Hz, 1H), 7.50 – 7.33 (m, 6H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.18 (q, *J* = 7.0 Hz, 1H), 4.43 (d, *J* = 13.0 Hz, 1H), 4.18 (d, *J* = 13.0 Hz, 1H), 1.66 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6, 139.4, 136.2, 134.5, 133.7, 131.0, 128.8, 128.6, 127.9, 127.4, 119.7, 52.1, 43.7, 16.3. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}BrNOS$ $[M+H]^+$: 348.0052, found: 348.0055.

7-Fluoro-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one ***(4e)*** : Colourless oil, 34.4 mg, yield: 60%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.1, 6.1 Hz, 1H), 7.47 – 7.34 (m, 5H), 7.03 – 6.98 (m, 2H), 6.20 (q, *J* = 7.0 Hz, 1H), 4.48 (d, *J* = 13.0 Hz, 1H), 4.22 (d, *J* = 13.0 Hz, 1H), 1.67 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.1 (d, *J* = 255.1 Hz), 163.1, 139.8 (d, *J* = 9.3 Hz), 139.6, 133.6 (d, *J* = 9.7 Hz), 128.8, 127.9, 127.4, 125.9 (d, *J* = 3.1 Hz), 113.8 (d, *J* = 24.1 Hz), 113.7 (d, *J* = 21.9 Hz), 51.9, 43.9, 16.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.2 (s). HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}FNOS$ $[M+H]^+$: 288.0853, found: 288.0852.

7-Chloro-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one ***(4f)*** : Colourless oil, 37.0 mg, yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.27 (m, 7H), 6.19 (q, *J* = 7.0 Hz, 1H), 4.47 (d, *J* = 13.0 Hz, 1H), 4.21 (d, *J* = 13.0 Hz, 1H), 1.67 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.1, 139.5, 139.0, 137.9, 134.1, 132.3, 128.7, 127.9, 127.4, 126.7, 126.5, 52.0, 43.7, 16.3. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}ClNOS$ $[M+H]^+$: 304.0557, found: 304.0557.

(3-(1-Phenylethyl)-7-(trifluoromethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one ***(4g)*** : Colourless oil, 43.8 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.34 (m, 7H), 6.21 (q, *J* = 7.0 Hz, 1H), 4.50 (d, *J* = 13.0 Hz, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 1.69 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.6, 139.2, 138.4, 133.31 (q, *J* = 32.9 Hz), 132.32, 131.5, 128.8, 128.0,

127.4, 124.2 (q, J = 3.9 Hz), 123.3 (q, J =271.4 Hz), 122.7 (q, J = 3.6 Hz), 52.2, 43.7, 16.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.3 (s). HRMS (ESI, *m/z*): calcd. for $C_{17}H_{15}F_3NOS$ $[M+H]^+$: 338.0821, found: 338.0825.

*7-Methyl-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one (**4h**)* : Colourless oil, 37.9 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 1H), 7.46 – 7.28 (m, 5H), 7.11 – 7.03 (m, 2H), 6.20 (q, J = 7.0 Hz, 1H), 4.43 (d, J = 12.9 Hz, 1H), 4.17 (d, J = 12.9 Hz, 1H), 2.36 (s, 3H), 1.65 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.9, 142.4, 139.9, 137.1, 131.0, 128.7, 127.7, 127.5, 127.1, 127.0, 51.7, 43.7, 21.4, 16.4. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104, found: 284.1108.

*7-Methoxy-3-(1-phenylethyl)-2H-benzo[e][1,3]thiazin-4(3H)-one (**4i**)* : Colourless oil, 43.0 mg, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 1H), 7.46 – 7.31 (m, 5H), 6.83 – 6.81 (m, 1H), 6.74 (s, 1H), 6.19 (q, J = 6.9 Hz, 1H), 4.45 (d, J = 12.9 Hz, 1H), 4.19 (d, J = 12.9 Hz, 1H), 3.84 (s, 3H), 1.65 (d, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.8, 161.9, 139.9, 139.1, 132.9, 128.7, 127.7, 127.4, 122.4, 112.6, 111.4, 55.6, 51.7, 43.8, 16.4. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1053, found: 300.1058.

*3-Butyl-2H-benzo[e][1,3]thiazin-4(3H)-one (**4j**)*[6a] : Colourless oil, 23.0 mg, yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.12 (m, 1H), 7.39 – 7.35 (m, 1H), 7.30 – 7.26 (m, 2H), 4.58 (s, 2H), 3.65 (t, J = 7.3 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.48 – 1.38 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.7, 137.0, 131.5, 130.7, 129.6, 127.1, 126.1, 48.6, 48.1, 30.2, 20.2, 13.9. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{16}NOS$ $[M+H]^+$: 222.0947, found: 222.0949.

*3-Benzyl-2H-benzo[e][1,3]thiazin-4(3H)-one (**4k**)*[6a] : Colourless oil, 30.6 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.9 Hz, 1H), 7.41 – 7.28 (m, 8H), 4.90 (s, 2H), 4.52 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.1, 137.1, 136.4, 131.8, 131.0, 129.3, 128.9, 128.1, 127.8, 127.2, 126.2, 51.1, 47.8. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791, found: 256.0793.

*3-Phenethyl-2H-benzo[e][1,3]thiazin-4(3H)-one (**4l**)*[6a] : Colourless oil, 36.0 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.23 (m, 8H), 4.36 (s, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.7, 138.9, 137.1, 131.6, 130.6, 129.5, 129.0, 128.7, 127.1, 126.7, 126.1, 51.2, 49.5, 34.8. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947, found: 270.0950.

*3-Cyclopentyl-2H-benzo[e][1,3]thiazin-4(3H)-one (**4m**)*[6a] : Colourless oil, 26.5 mg, yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.25 (m, 2H), 5.19 – 5.11 (m, 1H), 4.51 (s, 2H), 2.07 – 1.98 (m, 2H), 1.79 – 1.54 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.8, 137.2, 131.4, 130.9, 129.9, 127.1, 126.1, 54.8, 43.9, 29.3, 24.4. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{16}NOS$ $[M+H]^+$: 234.0947, found: 234.0952.

*Methyl 3-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)propanoate (**4n**)* : Colourless oil, 32.6 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.30 – 7.25 (m, 2H), 4.72 (s, 2H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.72 (s, 3H), 2.79 (t, *J* = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7, 164.0, 137.4, 131.7, 130.6, 129.3, 127.2, 126.1, 51.95, 50.2, 45.4, 33.4. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{13}NNaO_3S$ $[M+Na]^+$: 274.0508, found: 274.0506.

*3-Isopropyl-2H-benzo[e][1,3]thiazin-4(3H)-one (**4o**)* : Colourless oil, 24.8 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.26 (m, 2H), 5.09 – 5.02 (m, 1H), 4.51 (s, 2H), 1.27 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.4, 137.1, 131.4, 130.9, 129.9, 127.1, 126.1, 45.2, 42.5, 20.1. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}NOS$ $[M+H]^+$: 208.0791, found: 208.0797.

*Methyl 2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)propanoate (**4p**)* : Colourless oil, 31.1 mg, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.27 (m, 2H), 5.48 (q, *J* = 7.4 Hz, 1H), 4.81 (d, *J* = 13.0 Hz, 1H), 4.52 (d, *J* = 13.0 Hz, 1H), 3.77 (s, 3H), 1.59 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 163.9, 137.4, 131.9, 131.1, 128.9, 127.2,

126.1, 52.5, 52.35, 45.1, 15.5. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{13}NNaO_3S$ $[M+Na]^+$: 274.0508, found: 274.0508.

*Methyl 2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)pentanoate (**4q**)* : Colourless oil, 43.5 mg, yield: 78%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 1H), 7.41 – 7.37 (m, 1H), 7.31 – 7.27 (m, 2H), 5.44 (dd, *J* = 10.9, 5.0 Hz, 1H), 4.86 (d, *J* = 13.2 Hz, 1H), 4.46 (d, *J* = 13.2 Hz, 1H), 3.76 (s, 3H), 2.05 – 1.99 (m, 1H), 1.88 – 1.83 (m, 1H), 1.57 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.1, 164.4, 137.5, 131.9, 131.2, 129.0, 127.2, 126.1, 56.4, 52.4, 45.1, 31.2, 19.5, 13.5. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{17}NNaO_3S$ $[M+Na]^+$: 302.0821, found: 302.0828.

The larger scale reaction for the synthesis of benzooxathiin-4-imine 2a. A 350 mL Schlenk tube was charged with 2-methylthiobenzamide **1a** (0.543 g, 2.0 mmol), Ag_2O (0.232 g, 1.0 mmol), Selectfluor (0.709 g, 2.0 mmol), NaOAc (0.246 g, 3.0 mmol) and DCE (30 mL). The tube was then sealed in the heating mantle and stirred vigorously at 140 ˚C for 8 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (50 mL) and filtered through a pad of Celite. The filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2a** (0.315 g, 62% yield).

ASSOCIATED CONTENT

Supporting Information. ^1H, ^{19}F and ^{13}C NMR spectra of product **2**, **3**, **4**, the optimization of reaction conditions for benzothiazin-4-one **4a** and mechanistic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21572026 and 21702019), Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou University, and the Priority Academic Program Development of Jiangsu Higher Education Institutions. We also gratefully acknowledge NSF (CHE-1350541) and Indiana University Purdue University Indianapolis for financial support.

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